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Quantum-chemical Methods in Catalysis

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The methods and various approximations used in quantum-chemical studies of chemisorption and heterogeneous catalysis have been examined, and the principal directions and aims of these studies characterised. Particular attention has been paid to the concept of local centres in heterogeneous catalysis and its realisation in model quantum-chemical calculations. Various types of active centre on the surface of metals and oxides have been examined, and the questions of their quantum-chemical description discussed. Quantum-chemical calculations of the chemisorption and catalytic properties of the Bronsted and Lewis acidic centres of aluminosilicates and related systems have been reviewed.
The bibliography contains 90 references.

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I. INTRODUCTION

The theory of chemical catalysis is one of the most difficult fields of chemical science. Many problems of organic, inorganic, and metal-complex chemistry essentially converge here. In the case of heterogeneous catalysis, additional problems arise, since it is necessary to take account of the properties of the solid surface. It is possibly only in the last ten years that the extent of the structural complexity and the lability of the properties of the structure of solids has been fully appreciated. It is not surprising that the detailed experimental study of the mechanisms of heterogeneous catalytic reactions encounter considerable difficulties; the complex structure and variety of the active centres (even within a given system) controlling the reaction, their possible modification during the reaction, the variety of intermediate structures produced in the system, the superposition of different reaction channels, changes in reaction mechanisms, etc. all complicate the overall kinetic scheme and make it difficult to understand catalytic processes at the molecular level, so that their interpretation is usually not unambiguous.

The mechanisms of catalytic reactions are mainly studied by direct kinetic experiments (the study of non-stationary kinetic conditions is of particular interest). At the same time, the use of various physical methods to study catalytic systems is raising high hopes. Here, quantum-chemical calculations have been called upon to provide definite assistance.

The aim of the present review is not to provide a complete and systematic picture of the state of affairs in the application of quantum chemistry in catalysis. It is now impossible to do this in a single article, because of the large volume of published calculations. It is necessary to point out, however, that quantum-chemical calculations on individual systems are still fragmentary in character; different authors sometimes reach different conclusions, depending on the models of the active centres and the quantum-chemical methods used.

This feature is still a serious obstacle to the complete systematisation of the results of published studies. Subsequently, therefore, the present review will be restricted to a brief general characterisation of the principal aims and the methods used, and more attention will be paid to the concept of active centres. The review will make practically no reference to such important problems as the calculation of surface states and the rearrangement of the structure of the surface, chemisorption on elemental semiconductors, and lateral interactions of adsorbed molecules. The problems of calculations on chemisorption and reactions on metals will be dealt with to only a limited extent.

It should be emphasised that in the general theory of catalysis, in addition to quantum-chemical methods, whose role is extremely limited, use is made of the methods of statistics and thermodynamics, and physical and chemical kinetics. In addition, formal structural description, etc. is of considerable importance.

It is possible to distinguish three aspects of the application of the methods of quantum chemistry to catalytic systems. Firstly, quantum chemistry provides the most systematic language for describing the structure of catalytic systems and the processes taking place in them, at the electronic level. It is hardly possible at the present time to discuss the individual stages of a catalytic process without the concepts of reactions in σ- and π-electronic systems, covalent, ionic, and donor–acceptor bond types, etc. All this provides a basis for understanding the nature of the interactions in catalytic systems at a qualitative level of rigour, and this role of quantum chemistry cannot be underestimated, although it is often masked by specific applications. The possibilities provided by quantum chemistry in this area have not yet been exhausted.

It is possible to take as an example several approaches which in a number of cases may be useful and make it possible to reach simple qualitative conclusions comparatively easily. One of these can be described as the "modified" molecule method. In this case, the changes in the electronic structure of a molecule (the changes in the charges, the energies of individual bonds, etc.) brought about by contact with the catalyst are analysed. This method is used fairly widely in many studies, for example in a series of studies of acid–base reactions on oxides, carried out by the authors of the present review.[1-5]

This approach was developed further in studies[6,7] aimed at analysing the change in the vibronic interactions in molecules when they are coordinated to a catalyst. This approach gives a picture of the intramolecular forces acting on individual atoms and produced on coordination, so that it gives information on the possible deformations of the molecule and the tendency for changes to take place in various chemical properties. In studies of this type, the role of the catalyst reduces either to the transfer of an electron to the molecule or to the capture of an electron from the molecule; alternatively, a model functional group of the catalyst, for example H^+, OH^-, etc., is taken into account in explicit form in the calculation. In those cases where the influence of the adsorbent on the adsorbate is mainly electrostatic in character (for example a strongly heteropolar support or an individual charged centre), this influence can be estimated using simple electrostatic models.[8] For cubic ionic crystals it is possible to obtain explicit expressions for the electrostatic potential on a regular surface,[9] and in the more general case it is possible to use a system of point Coulombic charges.[10]

Another method of describing the influence of a catalyst on chemical transformations is based on the concept of boundary molecular orbitals. In this case, perturbation theory is usually employed. The application of this method to catalytic problems was developed in Refs.11 and 12.

Metal-complex systems have an important place in both homogeneous and heterogeneous catalysis. Thus in the qualitative quantum-chemical theory of catalysis, particular attention is paid to the analysis of coordinate bonding[13] and to a deeper understanding of the nature of such chemical bonds as the metal–carbene (or carbyne) bond, or M...H–C interactions, which are of considerable importance in catalysis. Here, various aspects of the coordinate bonding of hydrogen in metal complexes are acquiring particular importance.[14]

Secondly, specific applications of the methods of quantum chemistry to catalysis are associated primarily with the study of the elementary act of a given stage of the catalytic reaction, including the chemisorption (coordination) stage. The structural problems which arise in this case can be divided into the following three groups.

a) Calculations of the electronic structure of the assumed active centres (AC), which are generally various structural and impurity defects and surface functional groups. These include calculations of the change in the electronic structure of these active centres as a result of the chemical modification of the catalyst surface in various ways.

b) Estimation of the positions at which the chemisorption of atoms and molecules takes place, the geometry and energetics of chemisorption, comparison of the preference for different chemisorption states, and estimation of the magnitude of the energy barriers to transitions between these states. The investigation of the nature of chemisorption (molecular or dissociative, with or without activation), the determination of the degree of covalent and ionic character in chemisorption bonding, and analysis of the modification of these characteristics with change in the degree of coverage of the surface, etc., solution of the problem of the possible formation during chemisorption of structures with the transfer of ions or charged molecular fragments (carbonium ions, carbanions, etc.).

c) Direct analysis of different paths in the reactions of adsorbed molecules on a surface or in the reactions of adsorbed molecules with surface structures. Comparison of the Eley–Rideal and Langmuir–Hinshelwood mechanisms. Examination of the separate and combined mechanisms of a reaction and the study of the dependence of these channels on different forms of the catalysts, and the use of the results of the calculations for the planning of experiments.

Finally, a third important aspect of the application of the methods of quantum chemistry in catalysis is the calculation of the physical characteristics of surface centres. It was noted above that an important role is played by physical methods for studying catalysts, in particular spectroscopic methods: NMR, EPR, infrared, ultraviolet, photoelectron, X-ray electron spectroscopy, etc. The structural information provided by these studies is increased considerably when parallel quantum-chemical calculations are carried out. Extremely varied structural formations, which as yet have no direct analogues among traditional molecular structures, may be produced on a surface. The only approach, therefore, is to use the results of sufficiently correct quantum-chemical calculations.

Quantum-chemical calculations of chemisorption encounter a fundamental methodological difficulty associated with the need to take account of the interaction of a molecule with the unbounded surface of a solid. The initial stage of the development of the theory of chemisorption was characterised by increased attention to the purely solid-state characteristics of the system, and to the analysis of the types, symmetry, and properties of the zone surface states. This gave many important results; in particular, the conditions for the appearance of Tamm and Shockley surface states were determined. In this approach, ordered chemisorption was

regarded as a change in the structure of the surface states, and the adsorption of isolated molecules was regarded as the appearance of point defects on the surface with a tendency for the capture on this defect of an electron (or hole) from the band states of the solid. A detailed critical analysis of this problem has been carried out,[15] and it will not be dealt with further in the present review.

The development of experimental and theoretical studies of chemisorption led to the conclusion that chemisorption should be regarded rather as the formation of chemical surface compounds. In the theory of heterogeneous catalysis, this was reflected in the chemical concept of catalysis.[16] The determination of the local character of the electronic rearrangements taking place on chemisorption also influenced the quantum-chemical theory of chemisorption phenomena. The effort to obtain a correct description of local chemical bonds and the neglect of the effects of long-range order led to the development of the cluster approach, which involves the separation of a finite (usually small) fragment of the surface (cluster). This method makes it possible to use the methods of quantum chemistry directly.

The cluster approximation is very convenient in quantum-chemical calculations of surface structures. It makes it possible, without difficulty, to construct molecular models of all structural and impurity defects on a surface and models of surface functional groups, and to describe the surface of amorphous solids and alloys. The cluster approximation is also attractive in that it concentrates attention on the chemical nature of chemisorption and catalysis. This approach is now used in most studies involving the calculation of chemisorption. Different versions of the cluster approximation, its unsatisfactory features, and methods for improving its efficiency will be examined below. Various questions related to the choice of the "minimum" clusters for modelling active centres in heterogeneous catalysis have been discussed.[17]

II. QUANTUM-CHEMICAL METHODS

At the present time, practically the entire range of methods of quantum chemistry, from the simplest semi-empirical methods to fairly complete versions of the non-empirical approach, are used in quantum-chemical studies of chemisorption and surface structures. This situation appears justified, and should be preserved for a fairly long time. This is related, firstly, to the characteristic features of the systems studied: the cluster structures modelling the real surface are extremely extended molecular structures. Moreover, cluster modelling is always indeterminate. It is therefore usually appropriate to analyse a number of versions and to estimate the stability of the results of the calculations when the cluster is expanded; this makes it necessary to carry out a large number of individual calculations. All this requires the use of semi-empirical methods which are as economical as possible.

At the same time, situations often arise in which it is necessary to reach a sufficiently reliable conclusion. Such a situation arises, for example, in the analysis of the possibility of dissociative adsorption or when resolving the question of the reality of certain chemisorption structures. Although experimental methods are constantly improving, it is nevertheless the case that in such a complex and labile system as a surface, the investigation of a number of structural problems still cannot be carried out by experimental methods, and it is here that sufficiently reliable quantum-chemical calculations, carried out using non-empirical methods, may be useful. Moreover, the results of non-empirical calculations for small molecular systems can be used to select and improve the parametrisation of semi-empirical methods. This approach is finding increasing application in problems related to a surface.

Calculation schemes in quantum chemistry are traditionally based either on the method of molecular orbitals (MO) or on the valence bond method.[18] A molecular orbital ϕ_i is defined as a one-electron wavefunction describing the movement of an electron in the effective electric field of the nuclei and the other electrons. Usually, ϕ_i are represented as a linear combination (LCAO) of atomic orbitals (AO) χ_k

$$\varphi_i = \sum_k c_{ik}\chi_k \,, \qquad (1)$$

The many-electron wavefunction Ψ of a molecular system is expressed as the antisymmetrised product of the spin orbitals, and for closed levels it is conveniently represented as a Slater determinant. This approach is called the restricted Hartree–Fock (RHF) method. The analogous approach, in which the condition that the spatial parts of the spin orbitals ϕ_i^{α} and ϕ_i^{β} for electrons with spin α and β be equal is not imposed, is called the unrestricted Hartree–Fock method, and is often used in calculations for systems with open levels (free radicals, triplet and other states, etc.).

A fundamental shortcoming of the Hartree–Fock method is that it neglects the Coulombic correlation of the movement of the electrons. The calculation can be refined by the method of configuration interaction (CI), in which the complete wavefunction Φ is represented as the superposition of the Slater determinants Ψ for different configurations. With a sufficiently broad basis set in the expansion of Eqn.(1) and allowance for a large number of configurations, it is possible to carry out calculations with a high accuracy, and the accuracy of present-day calculations for small molecules already competes with that of experimental studies.

It is not the purpose of the present review to give details of quantum-chemical calculation schemes; see for example Ref.19. The treatment will therefore be restricted to a formal systematisation with particular attention to those methods which are fairly widely used in calculations on chemisorption and catalysis.

The group of simple semi-empirical MO LCAO methods includes the extended Hückel method (EHM),[20] and its modified form[21] in which additional allowance is made for core repulsion. In Ref.21, an attempt was made to obtain more justified values for the total energy, compared with the ordinary EHM method, in order to optimise the geometry of the molecular systems. This approach (the ASED method) was specially developed for problems of chemisorption and surface reactions, and has been used successfully in a whole series of subsequent studies (calculations of chemisorption and catalysis on metals). The application of the above form of the EHM to oxide systems, which have fairly high ionic character, is formally less justified, however.

The nex group of semi-empirical MO LCAO methods consists of the methods of so-called zero differential overlap. Here it is possible to distinguish two sub-groups, provisionally described as physical and chemical. The first consists of the CNDO/2 and INDO methods, and some of their modified forms.[19] These methods are oriented towards the calculation of electronic characteristics: charge distribution, dipole moments, polarisabilities, spin density, electronic spectra, etc.; that is mainly physical properties. The characteristic features of the parametrisation scheme in these methods make it possible, without particular difficulty, to extend it to the compounds of heavy elements, including 3*d*, 4*d*, and 5*d* transition elements (see for example Ref.22).

The second sub-group consists of the CNDO/BW and MINDO/3 methods, which are oriented towards the calculation of the total energy, heats of atomisation, barriers to conformational transformations, and the geometry of molecular systems. It is these characteristics that are particularly important and interesting in problems of chemisorption and catalysis, but the development of the parametrisation in this case involves much greater difficulties than in the first case. A parametrisation has now been described for the compounds of the elements of the second period (as far as fluorine). A simplified procedure has been proposed[23] for estimating the parameters in the CNDO/BW method, based on correlations with the parameters of the CNDO/2 method.

A parametrisation of the CNDO/BW method has been developed within the framework of the general scheme[24] for calculations on the chemisorption of compounds containing H, C, N, and O atoms on aluminosilicates. The CNDO/BW method gives good results in the calculation of chemisorption on oxides, mainly because this method provides a satisfactory description of hydrogen bonds. One significant shortcoming of the CNDO/BW method, however, is the unsatisfactory description of conjugated organic compounds, which makes it necessary to introduce special corrections. This shortcoming, generally speaking, is not shown by the MINDO/3 method, but the application of this method in chemisorption calculations requires expansion of the parametrisation to the elements of the third and subsequent periods. This problem has been solved for the Si and Al atoms in chemisorption on aluminosilicates.[25]

The problem of expanding the parametrisation of the MINDO/3 method to the 3*d* transition elements is now being studied by several research groups. Thus parameters have been proposed for calculating the chemisorption of hydrogen on iron[26] and on nickel.[27] The MINDO/3 method, however, provides an insufficiently good description of donor–acceptor bonds, particularly hydrogen bonds. In view of the above limitations of the CNDO/BW and MINDO/3 methods, it is appropriate, to control the reliability of the results, by carrying out parallel calculations by these methods.[25] Here, various control calculations carried out by non-empirical methods, and also by MNDO methods, may be of considerable assistance.

The next group of methods consists of calculation schemes in which use is made of a local approximation of the exchange potential: the X_α–SW and X_α–DV methods.[19] According to the formal classification, these methods occupy a unique intermediate position between semi-empirical and non-empirical methods. The X_α–SW method has proved to be extremely effective in calculations of ionisation potentials and electronic spectra, and it is now widely used for these purposes in the cluster analysis of the photoelectron and X-ray electron spectra of chemisorption structures. Certain characteristics of this method make it unsuitable, for example, for calculating the total energy and geometry of these structures. These same characteristic features, however, bring it closer to the methods used in most zone calculations in crystals. The X_α–DV method also gives fairly reliable results in the calculation of electronic spectra (although it is less economical than the X_α–SW method). The chief advantage of the X_α–DV method is that it is possible to carry out fairly good calculations of the energies and the geometry. Very powerful computers are required, however, to realise these possibilities. Nevertheless, the X_α–DV method is beginning to be more widely used in the calculation of surface structures and chemisorption.

Non-empirical (*ab initio*) methods form the apex of this quantum-chemical pyramid. Since with catalysis the main interest is in adsorbents containing many-electron atoms (for example transition metals and their oxides), it is appropriate, for the effective utilisation of non-empirical quantum-chemical calculations, to develop the pseudo-potential approximation for the electrons of the core. Most non-empirical calculations of chemisorption on metals are now carried out using this approach. The results of the first calculations using a pseudo-potential for aluminosilicates have now been published.[28] Another important task in non-empirical calculations is to take account of the correlation of the movement of the electrons. In addition to the traditional CI scheme, mention may be made of methods in which partial allowance is made for electron correlation. Among these methods, the generalised valence bond (GVB) scheme,[29] which is oriented towards the solution of problems related to surfaces and chemisorption, has found comparatively wide application in chemisorption calculations.

III. THE CLUSTER APPROXIMATION

The chief disadvantage of the cluster approach is the rupture of the chemical bonds between the bopndary atoms of the cluster and the rest of the lattice. This results in the production of artificial "surface states", situated partly in the band gap; distortion of the charge distribution; etc. Too many "surface" atome are obtained in the cluster. Unfortunately, to obtain a more correct surface/volume ratio, it is necessary to examine such large clusters that the approach loses its significance. The calculated characteristics of the electronic structure, in which the collective properties of the solid are important, converge slowly with increase in the size of the clusters. This applies to the energy of the Fermi level, the ionisation potentials, the electron affinity, and the atomisation energy.

The cluster approach is completely satisfactory, however, in the calculation of chemisorption, where a decisive role is played by local interactions. Thus even in the case of metals, which is particularly difficult for the cluster approach and where a band gap appears in the cluster calculation, chemisorption calculations for comparatively small clusters give good results. The preferred positions for the chemisorption of molecules, and the geometry, energy, and frequency characteristics of the chemisorption structures, are predicted fairly satisfactorily. Thus for example, in comparative calculations of the chemisorption of atomic hydrogen on Be, going from the Be_{22} cluster to Be_{36}, the changes in the equilibrium Be–H distance and the frequency of the stretching vibration of this bond are 4%, and the change in the energy of chemisorption ~20%. The relative stability of the chemisorption states is estimated correctly even for the Be_{13} cluster.[30]

To improve the results of the calculations, in addition to the obvious recommendation that the cluster be expanded, allowance for the influence of its environment, that is the rest of the lattice of the solid, can be proposed. A large number of recommendations of this kind have now been proposed and tested in the literature. This topic has also been reviewed.[31–33] The resulting hierarchy of versions of the cluster approximation makes it possible in principle to construct a bridge to band calculations.[32] At the same time, in the literature, particularly that dealing with chemical problems, use is generally made of simple model methods for taking account of the environment of the cluster; only these will be examined subsequently.

One of the first methods for taking account of the environment of a cluster was based on the introduction of boundary atoms, which were used to saturate the broken outer valence bonds of the cluster ("pendent valencies"). This method

was first used to calculate point defects in homoatomic crystals of diamond and silicon, and H atoms were used as the saturating atoms. The same approach was used successfully to calculate the chemisorption of atomic hydrogen on a graphite surface.[34] In Ref.23, an approach was developed in which the boundary valencies were saturated using univalent atoms whose quantum-chemical parameters (the form of the AO, electronegativity, etc.) were selected to give the best reproduction of various characteristics of the electronic structure of the solid (the stoichiometric charge distribution, the widths of the band gap and the valence band, the orbital composition of the top of the valence band and the bottom of the conductivity band, and various experimentally determined properties of the surface groups). These atoms bounding the cluster were called pseudo-atoms. Corresponding calculation schemes have been developed within the framework of the CNDO/BW[23] and MINDO/3[25] methods, and also the non-empirical method.[28]

This calculation scheme was first used[23] to describe the surface hydroxide groups of silica gel. The parameters of the pseudo-atoms A were selected to give the stoichiometric distribution of charge in a cluster imitating the "volume" of $Si(OA)_4$. The logical consistency of the scheme was verified by analysing the stability of the calculated electronic characteristics (charge distribution, position of the one-electron levels) with respect to expansion of the cluster, that is with successive replacement of the pseudo-atoms A in $Si(OA)_3$.[35] The results of the calculation of the infrared spectroscopic characteristics of the stretching vibrations of the OH bond in the cluster $(HO)Si(OA)_3$ show good agreement with experimental data in the range of both the fundamental ν_{OH} vibrational band and the overtones, and describe familiar trends in the properties of the OH groups of oxides, namely the comparatively weak dependence of ν_{OH} on the acidity of the surface OH group, and the marked increase in this dependence when basic molecules are adsorbed.[36]

Different versions of the scheme with boundary pseudo-atoms can be realised. Thus the orbitally stoichiometric cluster method[37] uses a boundary atom with one 3*s* or 3*p* or sp^3 orbital of the silicon atom with the AO oriented along the direction of the chemical bond.

Certain difficulties arise when attempts are made to extend the above scheme involving the introduction of boundary atoms into the cluster (which can be called the covalent cluster scheme) to lattices with high coordination numbers (Al_2O_3, MgO, ZnO, transition metal oxides). In this case it is more convenient to distinguish an ionic cluster, corrresponding to the ionic model of the lattice. In essence, excess (relative to the neutral cluster) electrons (or an electron deficit) are used to compensate the "pendent valencies", although in this case this terminology is of course fairly arbitrary. The resulting excess of electronic charge can be compensated, to obtain an overall neutral cluster, by an appropriate choice of the charge on the core of the boundary ions.[38]

For the discussion of these two methods of selecting the clusters (covalent and ionic), it is of interest to compare the results of calculations for a given system. This comparison has been carried out for the hydroxide group on an SiO_2 surface,[39] the magnetic resonance parameters of paramagnetic surface structures,[40] and a number of models of chemisorption.[41] In spite of certain differences, the two schemes on the whole give similar results. For more definite conclusions, it is necessary to carry out more extensive comparative studies. For close-packed oxide structures, in a number of cases, stoichiometric clusters (for example $Mg_{2n}O_{2n}$) will apparently be preferable, although in these cases also it is appropriate to take account of the Madelung field from the nearest part of the rest of the lattice.

Another method for selecting the cluster is based on the saturation of the "pendent valencies" within the cluster. This approach is convenient when comparing the chemisorption and catalytic activity of active centres of the same kind in different systems; it has been used successfully to compare the acidic centres in aluminosilicates and aluminium phosphates.[24]

IV. QUANTUM-CHEMICAL STUDIES OF CHEMISORPTION AND CATALYSIS ON METALS

The very first steps are now being taken in the quantum chemistry of catalysis on metals. This is revealed by the fact that the great majority of calculations deal with problems of chemisorption, and the problems of chemical transformations and catalytic reactions are as yet discussed only in a very few papers. From certain trends in the theoretical literature, however, a definite change towards chemical topics may be expected in the near future.

Various metals have been examined in the cluster approximation in quantum-chemical studies. The largest number of published theoretical studies deal with Li, Be, Al, Ni, Cu, and Pt, and to a lesser extent with Na, Fe, Ti, and Ag. The studies have for the most part dealt with the chemisorption of atoms (H, C, O, and various others), diatomic molecules (H_2, O_2, CO, N_2, NO) and simple organic molecules such as acetylene, ethylene, etc. Chemisorption at different positions on various faces of single crystals has been examined; for example, for the (100) face, atomic adsorption on an atom, on a bond, and in a four-coordinate C_{4v} position has been studied.

In a number of cases the question of the possibility of surface atomic adsorption and the estimation of the magnitude of the barrier to the transition from the state of an atom above the surface into the surface state has been discussed. An example is the non-empirical calculation of the adsorption of Li, O, and Na atoms on the (111) face of an Al crystal, which was modelled by a three-layer cluster Al_{19} with the (12, 6, 1) structure; the figures give the numbers of Al atoms in the individual layers.[42] The calculation was carried out using a pseudo-potential for the core electrons, so that each Al atom was modelled by a three-electron system (such an extended cluster could be examined only in this approximation). The calculations for $Al_{19}O$ were carried out for a system with C_{3v} symmetry with localisation of the O atom on the *z* symmetry axis perpendicular to the surface face of the cluster. Two local energy minima were found, corresponding to one chemisorption state situated above the surface and another situated under it, with octahedral coordination of oxygen. The two states have similar bond energies. The theoretical estimate of the energy of the transition below the surface for the oxygen atom (~2.4 eV), however, was much greater than the experimental estimate of this quantity (~1 eV). The discrepancy is apparently due to the fact that no allowance was made for electron correlation. In the case of Li and Na atoms, no chemisorption bound states were found below the surface. Another example of studies of this kind is provided by Ref.43, where the X_α–DV method was used to calculate the adsorption of S, Se, and Te atoms on Ni clusters modelling the (100), (110), and (111) faces.

In calculations of the adsorption of diatomic (and polyatomic) molecules on metals, the question of the dissociative adsorption and fragmentation of the molecules is of particular interest for catalysis. These topics for the most part have been examined using semi-empirical methods of calculation. An illustration is provided by Ref.44, where the CNDO/2 method was used in cluster calculations of the dissociative

chemisorption of H_2 on Ni, and also Ref.45, where the dissociative chemisorption of O_2 on Ni was examined by the EHM. In those cases where there is a good pseudo-potential approximation for the core electrons, however, it is also possible to carry out non-empirical calculations of this type. For example, the decomposition of methanol on Ni(100) has been examined,[46] and the calculation was carried out by the GVB method for an Ni_{20} cluster. The results of quantum-chemical calculations have also been used[47] to study the role of the *d*-orbitals of metal atoms in the dissociative adsorption of hydrogen on metal surfaces.

Of the published papers on the theoretical study of the fragmentation of organic molecules on metal surfaces, mention may be made of work[48] in which the original form of the EHM was used to examine the localisation of different hydrocarbon fragments (CH_n and $C-CH_n$, where $n = 1, 2, 3$) on the (111) face of a Pt single crystal. The calculation was carried out in the cluster and band versions; it was concluded that allowance for band effects has no significant influence on the results of the calculations. From a comparison of the energies of different chemisorption states for these fragments, the authors cited[48] arrived at the so-called covalent model of chemisorption bonding, in which the most favourable structures are those with complete saturation of the valence of the hydrocarbon fragments; thus for example for CH, CH_2, and CH_3, three-, two-, and one-coordinate states with respect to the platinum atoms are produced.

The quantum-chemical study of the electronic structure and chemical properties of adsorbed atoms and other structural defects such as steps and vacancies is of particular interest for the discussion of the catalytic properties of metal surfaces. It is widely held that these structures play a unique role as active centres in catalysis. Thus cluster quantum-chemical calculations have shown that certain characteristic features of the electronic structure of the adsorbent, which favour the reactions, can be related to the presence of adsorbed atoms. Thus in a cluster calculation by the X_α–DV method it was found[49] that an adsorbed Fe atom on the Fe(111) surface leads to the appearance of new occupied states of *e* symmetry close to the Fermi level, and this may facilitate the dissociation of the CO molecule; this effect was not detected for the adsorption of a Cu atom on Cu(111).

The increased chemical activity of step defects on a Pt surface has been discussed in work[50] where the X_α–SW method was used. The calculation shows clearly that these defect structures are coordinatively unsaturated; in the electronic spectrum, a number of orbital states are identified, which lie close to the top of the valence zone and which are directed "away from the surface". The increased chemisorption and catalytic activity of step defects on a surface can also be related to the appearance of these unsaturated valences.

The production of centres with increased activity on metal surfaces may be related not only to structural defects but also to chemical impurities. The influence on the chemisorption of O_2 of atomic oxygen in the surface region of Ni(111) has been examined.[45] It was found that in this case there should be a change in the order of preference of adsorbed states, and the most favourable state is one-point adsorption with perpendicular orientation of the molecule. This example of course indicates only that this influence exists, but it may also appear in catalysis.

A cluster calculation (ASED method) of the dissociative adsorption of CO in Ni(111) has been carried out[51] to determine how the dissociation is influenced by the modification of the surface by electron-donor (K, Na) and electron-acceptor (Cl, S) additives. It is known from experiments that the former activate and the latter inhibit the process. The authors cited examined Ni clusters into which a K or Cl atom was introduced, leading to qualitatively different changes in the energy profile along the reaction path; the effect was significant only when the modifying atom entered the immediate environment of the active centre, that is it is fairly local in character. From the qualitative viewpoint, the presence of, for example, the K atom leads to greater population of the MO of the nickel cluster from which, during the chemisorption of CO, partial transfer of electron density takes place to the antibonding $2\pi^*$ orbital of the CO moelcule, facilitating its dissociation. Thus the calculation predicts the production of a negative charge on the CO molecule and an increase in its bond length in this adsorption.

The role of modifying additives may be played by adsorbed reagents, intermediate complexes, and reaction products. This is probably one way of influencing the composition of a reaction mixture during a catalytic reaction on a surface. This provides extensive possibilities for the application of the methods of quantum chemistry. Thus quantum-chemical calculations can be used to look for chemisorption states with an increased chemical activity; an example is provided by a study[52] where a cluster calculation (GVB method) was used to find a quasi-radical adsorption state of an O atom on an Ni surface.

As noted above, there are only a few published papers on the quantum-chemical examination of surface reactions on metals. A typical example is provided by a study[53] where the ASED method was used to calculate the adsorption of CO and O on Pt(111); the calculation was carried out for Pt_4 and Pt_9 clusters. The Langmuir–Hinshelwood and Eley–Rideal mechanisms for the reaction $CO + O \rightarrow CO_2$ were compared. It was concluded that the energy characteristics of the two reaction channels are similar; the estimated magnitude of the activation energy for the formation of CO_2 from adsorbed CO and O was ~1.6 eV, which is close to the experimental value (~1 eV). The chemisorption of Cl, Cl_2, and HCl on Fe(100) and the reaction $HCl + O(s) \rightarrow OH(s) + Cl$, where (s) represents the surface form, has also been discussed;[54] the surface was modelled using Fe_n clusters, where $n = 4-21$.

In conclusion it may be noted that the published results of quantum-chemical calculations, together with the results of experimental studies, are sometimes used for a general analysis of important classes of catalytic reaction. An illustration is provided by the discussion of the catalytic hydrogenation of CO on transition metals.[55]

V. QUANTUM-CHEMICAL STUDIES OF CHEMISORPTION AND CATALYSIS ON OXIDES

In this section, particular attention will be paid to chemisorption and catalytically active centres on the surface of silica and aluminosilicates. Other oxides will be discussed only briefly. This to some extent reflects the thematic distribution of quantum-chemical studies in this field.[56] A series of studies involving quantum-chemical calculations of adsorption on SiO_2 can be considered first. Fig.1 shows different possible forms of the adsorption of an H_2O molecule on SiO_2. The relative stability of the two forms of H_2O adsorption on a terminal OH group in silica gel has been debated in the literature. A semi-empirical calculation by the CNDO/BW method using a cluster scheme with boundary pseudo-atoms[23] led to the conclusion that form (I) is preferred, in qualitative agreement with experimental data which show that there is only slight perturbation of the frequency characteristics of the hydroxide group when water is adsorbed. A different result was subsequently obtained by

a non-empirical STO-3G calculation.[57] It should be noted, however, that H atoms were used as boundary atoms in the cluster.

The development of a scheme for including pseudo-atoms in non-empirical calculations[28] made it possible to carry out an improved version of this study. This confirmed the conclusion reached in the semi-empirical calculation. The same conclusion was reached in calculations of the adsorption of H_2O on a terminal hydroxide group in SiO_2.[58] In this case, the CNDO/2 method with gradual increase in the size of the clusters was used.

Systematic calculations of the adsorption of H_2O on geminal and vicinal pairs of OH groups in silica gel have been undertaken.[59] The energy of the chemisorption of an H_2O molecule on a hydroxide group in silica was estimated as ~10 kcal mole^{-1}. The question arose of whether the adsorption of H_2O on a silicon atom is energetically more favourable (form (IV) in Fig.1). Non-empirical calculations[28,60] do not indicate that chemisorption of H_2O and NH_3 at an Si atom is possible (as is sometimes assumed). This chemisorption becomes favourable only when there is appreciable deformation of the geometry of the silicon–oxygen tetrahedron (increase in the length of the Si–O bonds, increase in the O–Si–O valence angle), that is only on highly defect structures or on specially prepared surfaces. This apparently provides the answer to the question, discussed in the literature (in the interpretation of experiments and the results of different quantum-chemical calculations), of the production, stability, and prevalence of this form of coordination bonding of H_2O on silica. The details of this discussion cannot be examined in the present review, but references to this topic can be found in Refs.28 and 60.

The CNDO/BW calculation scheme described above has been used[61] to calculate the chemisorption of NH_3 at a hydroxide group in SiO_2. In this case the most favourable form of adsorption corresponds to the production of a hydrogen bond between the nitrogen atom of ammonia and the hydrogen atom of the surface hydroxide group. The calculation on the whole shows good agreement with the results of infrared spectroscopic studies of the adsorption of NH_3 on silica. The adsorption of the molecules of thiophene and thiophane on silica has been calculated[62] by the CNDO/2 method.

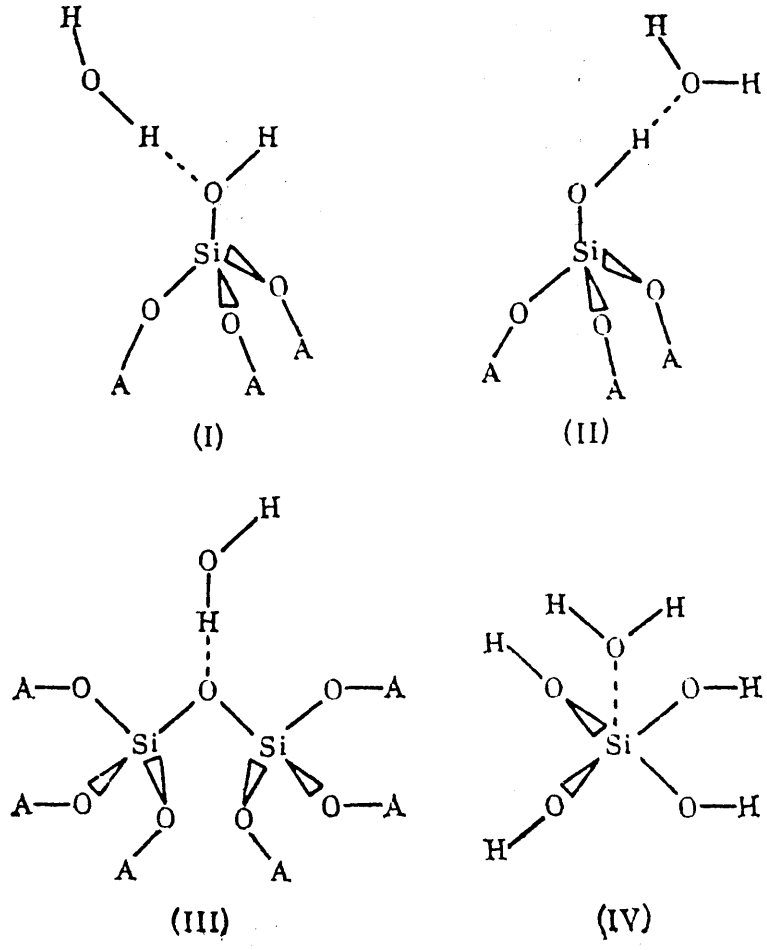


Figure 1. Cluster models of the possible forms of adsorption of H_2O on an SiO_2 surface; here and subsequently, A represents a univalent pseudo-atom.

Quantum-chemical calculations of the synchronous mechanism of the surface reactions of isotopic H/D exchange between a terminal OH group in SiO_2 and molecules of water and hydrogen have been carried out.[23] A systematic study of the influence of change in the acidity of the hydroxide group on the reaction of isotopic H/D exchange with water has been carried out.[63] The most important conclusion from these studies was that the energy barriers of these mechanisms are comparatively low, so that these processes can take place at low temperatures. It was found that the lowest energy corresponds to a transition state with C_{2v} symmetry (compared with C_{3v} symmetry). The extension of this conclusion to other systems indicated, for example, that isotropic exchange between the hydroxide group and an acetylene molecule (where the formation of a C_{2v} transition state is possible) should take place more readily than the corresponding reaction with an ethylene molecule (where only a C_{3v} transition state can exist); this conclusion was subsequently confirmed by direct calculation.[64] The qualitative dependence of these mechanisms on the acidity of the surface group and on the properties of the molecule, obtained in these quantum-chemical calculations, may indicate directions for experimental studies.[63]

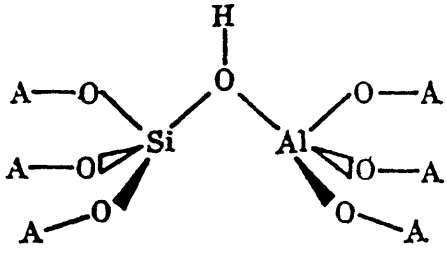


Figure 2. Cluster model of a Bronsted acidic centre in an aluminosilicate.

Quantum-chemical studies of the Bronsted acidic centres (BAC) and Lewis acidic centres (LAC) in aluminosilicates can now be considered. The simplest cluster that can be used to describe a bridging hydroxide group in aluminosilicates is shown in Fig. 2. The results of the calculation show that this group should have much stronger acidic properties than a terminal OH group in SiO_2 (estimated from the energy of removal of a proton). In the cluster calculation it was shown that change in the chemical composition of the second sphere (relative to the OH group; for example, by replacing Si by Al + H) leads to an appreciable decrease in the acidity of the OH group; this calculation naturally requires expansion of the cluster shown in Fig. 2. Systematic calculations of this kind, together with allowance for Loewenstein's rule, made it possible to interpret the change in the Bronsted acidity in a series of zeolites with different Si/Al ratios.[65]

Cluster calculations (CNDO/BW method) of the chemisorption of H_2O [59] and NH_3 [61] on bridging OH groups in aluminosilicates have been carried out. A non-empirical method has been used[66] to calculate the chemisorption of H_2O on the bridging groups in aluminosilicates. It may be noted that even in the case of the adsorption of the strong base NH_3 on an acidic bridging hydroxide group, the calculation does not indicate that the formation of an isolated NH_4^+ ion (that is transfer of a proton to NH_3) is possible. Preliminary results indicate that this form can be stabilised only by the two-point adsorption of NH_4^+ on basic centres of the surface. This indicates the possibility of the easy formation of carbonium ions in these systems, often postulated in the discussion of the mechanisms of acid catalysis. At low degrees of covering, when the effects of solvation in the adsorption layer can be neglected, proton transfer to organic molecules (alcohols, alkenes) should apparently require appreciable expenditure of energy. This in turn raises the question of the possible competition from a synchronous mechanism in these reactions, particularly at lower temperatures.

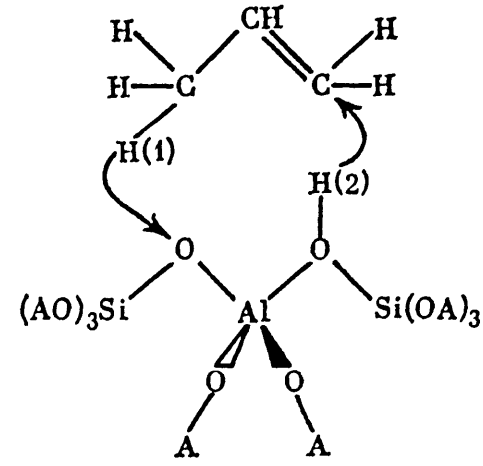


Figure 3. Cluster model of the mechanisms of the isomerisation of propylene on an aluminosilicate surface.

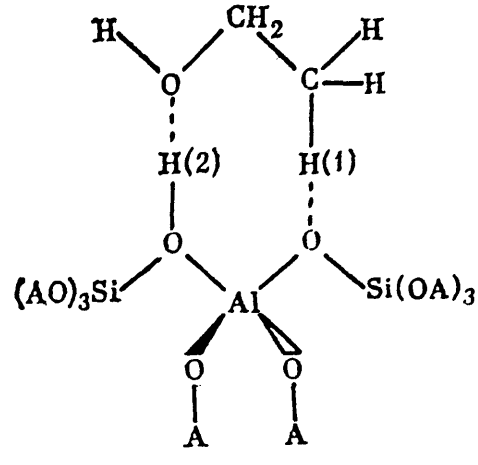


Figure 4. Cluster model of the synchronous mechanism of the dehydration of C_2H_5OH on an aluminosilicate surface.

The carbocation, carbanion, and synchronous mechanisms of the displacement of the double bond in alkenes, catalysed by a birdging hydroxide group in aluminosilicates, have been compared.[67] The cluster examined is shown in Fig. 3; the carbocation mechanism corresponds to the initial displacement of the atom H(2), the carbanion mechanism to the initial

displacement of the atom H(1), and the synchronous mechanism to their simultaneous displacement. The synchronous mechanism of the dehydration of ethanol on the same BAC (Fig.4) has been examined.[68]

As noted above, the most interesting conclusions from these studies are those on the possibility (or difficulty) of the synchronous mechanisms, the factors favouring them (for example the appropriate geometry of the adsorption centre), and the prediction of various qualitative relationships. The latter include, for example, the conclusion that these mechanisms depend comparatively little on the acidity of the hydroxide group; this can be understood qualitatively if account is taken of the fact that the synchronous mechanism involves an acid–base pair, and that a change in acidity in one direction produces changes in the opposite direction in the characteristics of the basic centre, so that there is effective compensation.

The theoretical estimation of the relative specific catalytic activity (within a given system) of different active centres of the same kind, for example BAC, having different structures, is of undoubted interest for catalysis. In addition to a comparison of the strengths of different active centres, this also requires the estimation of their relative concentrations, and definite information on the mechanism of the reaction. The first attempt of this kind at a semi-quantitative level was made[69] in a comparison of BAC of three types in aluminosilicates: a bridging hydroxide group, a water molecule coordinated to an Al atom, and an adsorbed hydroxonium ion. A cluster scheme was used for this calculation. It was concluded that the first two BAC have comparable activities, whereas the concentration of hydroxonium ions is too low. All the studies were carried out for the dehydration of butanols. A quantum-chemical study of different possible BAC in aluminium phosphates, with analogous formulation of the problem,[70] led to the conclusion that the formation of bridging hydroxide groups in these systems is unlikely. In agreement with experiment, the calculation predicts the formation of terminal P–OH groups in these systems. The cluster approach was used to compare the strengths of the BAC in aluminosilicates and aluminium phosphates, and it was concluded that the bridging OH group in aluminosilicates is more acidic than the P–OH group in aluminium phosphates.

A separate series of studies deal with the cluster modelling of the LAC in aluminosilicates.[71–73] It was shown that the exposed three-coordinate Al(1) atom in the pyramidal configuration (see Fig.5) shows all the characteristic properties of an LAC;[72] It has a low-lying unoccupied orbital, localised mainly on Al, and it shows qualitatively the chemisorption properties characteristic of LAC. Estimation of the energies of both molecular and dissociative adsorption on this centre (for H_2O, NH_3, and CH_3OH molecules), however, gave an unexpectedly high value (several hundred kJ $mole^{-1}$). The calculation was carried out by the CNDO/BW method. Non-empirical estimates led to essentially the same conclusion.

As noted subsequently,[73] however, the chemisorption properties of Al in an oxide lattice may change considerably as a result of the structural coordination of anions. It is possible to have a situation in which only activated adsorption is realised. This last case is illustrated in Fig.5; the localisation of Al in position 2 is energetically more favourable, due to the structural coordination of Al in the lattice. An adsorbed molecule can stabilise the Al atom in position 1, but the change Al(2) → Al(1) generally requires passage over an energy barrier.

It is thus possible to reach the general conclusion that the types of LAC depend markedly on the rigidity of the lattice, and that there is probably extensive dispersion of the properties of the LAC even within a given system; the conclusion that activated adsorption is possible may be the subject of directed experimental studies. A comparison of the strengths of the structural coordination of Al in aluminosilicates and aluminium phosphates[70] indicated that the LAC are stronger in aluminosilicates.

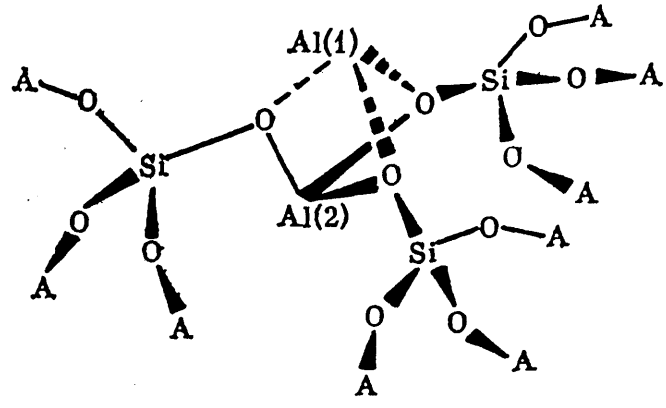


Figure 5. Cluster model of a Lewis acidic centre in an aluminosilicate.

The development of the concepts of structural non-rigidity in the systems being considered made it possible to approach in slightly non-traditional fashion the question of the quantum-chemical estimation of the thermal stability of zeolites.[74] Here, the usual approach involves the isolation of the weakest element of the structure. In zeolites, this element is the donor–acceptor bond Al...O. In quantum-chemical calculations, the difference in the strengths of the Si–O and Al–O bonds is revealed, for example, in the difference in the Wiberg indices P of these bonds. By calculating the change in the Wiberg indices P_{AlO} for different forms of zeolite structure, it should be possible to follow the nature of the change in the stability of the zeolite structure. This approach was widely used, for example, in a series of studies[75–78] on the cluster modelling of the structural rings in zeolites, where the influence of the chemical character of the central cation and its effective charge were examined. Although this approach undoubtedly has advantages, it essentially ignores the fact that the stability of a given structure is determined not only by its strength but also by the presence (or absence) of other structural conformations with similar energies.

The examination of the problem of the thermal stability of zeolites by comparing the energies of competing structures opens up new possibilities;[74] in particular, it leads immediately to the conclusion that boralites are less stable than zeolites.

Another type of active centre in zeolites may be cations in cation positions (zeolite windows of different types). These centres have been the subject of an extensive series of studies by Beran and co-workers.[76–78] The calculations were carried out by the CNDO/2 method, and clusters modelling the four- and six-membered "windows" in zeolites and the cations inside them were examined. It is not possible to analyse this entire cycle of studies in the present review; some references to these studies have been given above, and they are examined in more detail in Ref.33.

Finally, brief mention may be made of quantum-chemical calculations on active centres, chemisorption, and reactions in other oxides. As already noted, the cluster modelling of the surface centres of oxide lattices with high coordination numbers encounters certain difficulties. (This feature apparently explains the comparatively small number of calculations of this kind.) An example of this type is the Al_2O_3 surface. In this case, quantum-chemical methods have been used to study the properties of the surface hydroxide groups, and also LAC, associated with surface oxygen vacancies. An orbitally stoichiometric cluster, combining Al atoms in octahedral and tetrahedral positions, was used[79-81] to study various surface defects and their chemisorption properties. It was established that the formation of oxygen vacancies leads to the appearance of LAC. The adsorption of H_2O, HF, KOH, and NH_3 was examined. The calculation showed that fluorination increases the strength of the Lewis activity, whereas the addition of alkali and ammonia weakens it, in agreement with the experimental data. The same approrch was used[81] to examine the dependence of the Lewis acidity on the degree of dehydroxylation of γ-Al_2O_3.

Different defect centres in Al_2O_3 have been discussed[82,83] using simple ionic clusters and the EHM and the X_α–SW method. Cluster calculations (CNDO/2 method) and a simple qualitative quantum-chemical scheme have been used[24] to carry out a systematic examination of the dependence of the frequency of the ν_{OH} stretching vibrations of the surface hydroxide groups on Al_2O_3 on their immediate environment. The cluster approach (CNDO/2 method) has been used[84] to calculate the chemisorption of ethanol on γ-Al_2O_3; molecular adsorption and two forms of dissociative adsorption were examined.

The possibility of the dissociative adsorption of H_2 on an MgO(001) surface has been discussed;[85] the calculations were carried out by a non-empirical method using a minimum ionic cluster. Account was taken of the Madelung field. It was concluded that the dissociation of H_2 on a defect-free MgO surface is impossible.

Transition metal oxides form a large and important class of catalysts. Quantum-chemical calculations of the surface centres and reactions on these systems are only beginning. Examples include the examination of clusters modelling the V^{5+} ion in a tetrahedral and octahedral environment of oxygen ions.[86,87] In these studies, the nature of the electron rearrangements taking place on excitation into the singlet and triplet states was analysed. This problem was formulated in relation to various problems in photocatalysis.

An attempt has been made[88] to use the cluster approach to study the reaction of NO with NH_3 on a vanadium oxide surface; the CNDO/2 method was used. Different chemisorption structures and a successive series of states along the reaction path were examined; it was concluded that the Eley–Rideal mechanism applies. An unsatisfactory feature of the calculation is that the "pendent valencies" of the cluster were saturated using H atoms, which can hardly be justified for this system. The fact that the results did not change significantly on going to a larger cluster, however, indicates that the qualitative conclusions are correct.

Deposited systems may provide an extensive field of application for quantum-chemical methods, but few studies have as yet been carried out.[89,90]

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To summarise, it can be stated that the application of the methods of quantum chemistry in the theory of surface phenomena and catalysis has now developed into a separate branch of science with its own methodology, experience, success, and failure. This field is now being very actively developed. It is faced with severe methodological problems, associated with the need to improve the calculation schemes (in particular the cluster approximation) and to increase the efficiency of the programs (primarily for non-empirical calculations and calculationd by the X_α–DV method). Considerable effort is also required to determine the optimum directions for these studies in catalysis. The latter to a large extent depends on progress in the experimental study of the mechanisms of catalytic reactions, and should be carried out in close contact with experiment.

An increase in the mutual influence of quantum-chemical and kinetic studies can be expected. The greatest problems and the greatest progress in the application of quantum-chemical methods in the study of chemisorption and catalysis are undoubtedly still in the future.

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